

CLAIMS

1. The combination of ingredients, especially for use in the formulation of a one or two-pack retroreflective ink, comprising retroreflective elements, microbeads additional to said retroreflective elements and/or constituting said retroreflective elements at least in part, binder chemicals for attaching the retroreflective elements and microbeads to a substrate to which the ink is to be applied, and a coupling agent for coupling the microbeads and cross-linking the binder chemicals, the coupling agent being unreactive until the printing process is carried out.
2. The combination of Claim 1 in which the coupling agent is unreactive except at elevated temperature at which the printed substrate is cured.
3. The combination of Claim 1 or 2, at least some of the microbeads being without a retroreflective coating.
4. The combination of Claim 1, 2 or 3 in which the binder/coupling agent system is selected from the group comprising:
  - polyvinylidene chloride copolymer as binder and (3-aminopropyl) silanetriol and/or blocked 1, 6 hexamethylene diisocyanate trimer as coupling agent;
  - an acrylic copolymer as binder and (3-aminopropyl) silanetriol and/or blocked 1, 6 hexamethylene diisocyanate trimer as coupling agent; and
  - polyurethane as binder and blocked 1, 6 hexamethylene diisocyanate trimer as coupling agent.
5. The combination of any one of Claims 1 to 3 further comprising one or more components selected from the group comprising:

pigment; humectant, optionally urea and/or 2,3 propane diol; buffer, optionally based on ammonium or sodium phosphates; dispersant; defoamer; thickening agent; cross-linking agent; softening agent; carbon black; UV absorbing material; anti-scuffing agent, optionally a silicone or fluoropolymer; light spill-suppressing agent; anti-static agent and water repellent agent, optionally a silicone or fluoropolymer.

6. The combination of any one of Claims 1 to 5 in which the binder volume to bead volume ratio is equal to or less than 50%.
7. The combination of any one of Claims 1 to 6 in which the microbeads are all or essentially all unmetallised and the retroreflective elements comprise reflective flake particles.
8. The combination of any one of Claims 1 to 7 in which the binder forms at least part of a liquid carrier medium in which the retroreflective elements and/or microbeads are incorporated.
9. The combination as claimed in any one of Claims 1 to 7 in which the binder chemicals and retroreflective elements/microbeads comprise one pack retroreflective ink or a two-pack retroreflective ink with the coupling agent comprising the second pack.
10. The combination of Claim 9, being a two pack ink in which the coupling agent comprises a reactive polyisocyanate and/or an alkoxysilyl alkyl derivative.
11. The combination of any one of Claims 1 to 10, the microbeads having silicate (optionally sodium silicate) and/or silane (optionally an amino silane such as bis-[gamma-(trimethoxysilyl) propyl] amino) and/or stannous chloride applied thereto.

12. The combination of Claim 11 in which the microbeads are metallised, optionally with a coating of aluminium, the metal being superposed on the stannous chloride.
13. The combination of Claim 11 or 12 in which the microbeads are metallised, optionally with a coating of aluminium, the silicate and/or silane being superposed on the metallised beads and the silane where present being superposed on the silicate where present.
14. A one or two-pack retroreflective ink comprising the combination claimed in any one of Claims 1 to 13.
15. An ink as claimed in Claim 14, being water-based.
16. An ink as claimed in Claim 14 or 15, formulated suitably for screen printing.
17. An ink as claimed in Claim 14, 15 or 16 of which the viscosity is less than or equal to 40 pascals, preferably between 10 and 30 pascals, at room temperature.
18. Microbeads for use in the production of a retroreflective ink, the microbeads having silicate (optionally sodium silicate) and/or silane (optionally an amino silane such as bis-*[gamma-(trimethoxysilyl) propyl] amino*) and/or stannous chloride applied thereto.
19. Microbeads as claimed in Claim 18 which are metallised, optionally with a coating of aluminium, the metal being superposed on the stannous chloride.

20. Microbeads as claimed in Claim 18 or 19 which are metallised, optionally with a coating of aluminium, the silicate and/or silane being superposed on the metallised beads and the silane where present being superposed on the silicate where present.

21. Microbeads as claimed in any one of Claims 18 to 20 having one or more of the following characteristics: a refractive index in the range of 1.8 to 2.2, preferably about 1.9; in the form of beads having a median size in the range of 10 to 100 microns, preferably 25 to 70 microns; and composed of titanium/barium glass.

22. A retroreflective ink containing microbeads as claimed in any one of Claims 18 to 21

23. An ink as claimed in Claim 22 including binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied.

24. An ink as claimed in Claim 23 including a coupling agent for coupling the microbeads and cross-linking the binder chemicals, the coupling agent being unreactive until the printing process is carried out.

25. A method for making a one-pack retroreflective ink comprising the steps of:

- making microbeads;
- suspending the microbeads in a liquid carrier medium;
- the liquid carrier medium comprising binder chemicals for attaching the microbeads to a substrate to which the ink is to be applied and a coupling agent which couples the microbeads and cross-links the binder chemicals, the coupling agent being unreactive except at elevated temperature at which the printed substrate is cured.

26. A method according to Claim 25, comprising applying an aluminium coating to the microbeads.
27. A method according to Claim 26, comprising pre-treating the microbeads with stannous chloride prior to application of the aluminium coating.
28. A method according to Claim 27, in which the microbeads are treated with a dilute aqueous solution of stannous chloride.
29. A method according to any one of Claims 25 to 28, in which the microbeads are hemispherically metallised in a vacuum metallising process in which they are held on a film, optionally a polyester or polyolefin film, with an adhesive coating for transport through the metallising process, the adhesive coating comprising a styrene/butadiene type adhesive.
30. A method according to Claim 29 in which, following metallisation, the film is passed through an aqueous solution of citric acid.
31. A method according to Claims 29 or 30 in which the film is treated ultrasonically to assist in release of the microbeads from the adhesive surface.
32. A method according to any one of Claims 28 to 31 in which the microbeads are treated prior to inclusion in the ink with a silicate, optionally a dilute aqueous solution of sodium silicate.
33. A method according to any one of Claims 25 to 32 in which the microbeads are treated with a silane, preferably an amino silane, prior to inclusion in the ink.

34. A method according to Claim 32 or Claim 33 when dependent on Claim 29 in which the microbeads are treated with the silane, optionally an amino silane such as bis-[*gamma*-(trimethoxysilyl) propyl] amine, following the silicate treatment.

35. A method according to any one of Claims 25 to 34 in which an amino silanetriol, e.g. an amino silane, and/or a blocked polyisocyanate is added to the liquid carrier medium as coupling agent.

36. A method according to any one of Claims 25 to 35, in which a liquid carrier medium is prepared comprising binder chemicals and coupling agent, and the microbeads are added to the medium.

37. A method according to Claim 36, in which a further additive or additives are incorporated in the liquid carrier medium, said additives being selected from the group comprising:

pigment; humectant, optionally urea and/or 2,3 propane diol; buffer, optionally based on ammonium or sodium phosphates; dispersant; defoamer; thickening agent; cross-linking agent; softening agent; carbon black; UV absorbing material; anti-scuffing agent, optionally a silicone or fluoropolymer; light spill-suppressing agent; anti-static agent and water repellant agent, optionally a silicone or fluoropolymer.

38. A method according to Claim 37, in which a thickener is added to the liquid carrier medium in two steps, namely before and after the addition of the binder and coupler.

39. An ink produced by the method of any one of Claims 25 to 38.

40. A substrate coated or printed with ink as claimed in any one of Claims 14 to 17, 22 to 24 and 39.
41. A substrate as claimed in Claim 40 in the form of a screen for displaying projected images or a studio background for chroma-keying applications.
42. A substrate as claimed in Claim 40 in the form of flexible tape.
43. A method of providing a substrate with a retroreflective coating comprising applying to the substrate an ink as claimed in any one of Claims 14 to 17, 24 and 39, the ink having been formulated as a one-pack ink and the coupling agent being activated after the ink has been printed or coated on to the substrate.
44. A method as claimed in Claim 43 in which the coupling agent is activated by curing of the ink coating at elevated temperature.
45. A method as claimed in Claim 43 in which the coupling agent is activated by UV light or other high energy radiation during and/or after the printing process.
46. A retroreflective one-pack ink with a storage life of not less than 3 months, preferably not less than 6 months and more preferably not less than 12 months.
47. A retroreflective one-pack ink which has a viscosity of between 10 and 30 pascal after storage for not less than 3 months, preferably not less than 6 months and more preferably not less than 12 months.
48. A retroreflective one-pack ink which has laundering durability such that retroreflectivity is not reduced by more than 40% (preferably by not more than 30%,

more preferably by not more than 20%) when applied to a substrate in the form of a cotton, nylon or polyester fabric and laundered for 5 cycles in accordance with ISO 6330, method 5A.

49. A fireproof or fire retardant fabric printed or coated with a retroreflective ink which comprises retroreflective elements in a polymeric matrix, the fabric comprising a structural component that chars before it melts.

50. A fabric according to claim 49 made fireproof or fire retardant by application of a fire retardant agent.

51. A fabric according to claim 50 in which the fire retardant agent comprises Proban ® or Pyrovatex ® or a like agent, applied to a cellulosic.

52. A fabric according to any one of Claims 49 to 52, the fabric comprising an aramid fibre.

53. A fabric according to any one of Claims 49 to 52, in which the ink is non-burning once applied to the fabric.

54. A fabric according to claim 53, in which the ink is aqueous-based and the polymeric matrix comprises polyvinylidene chloride.

55. A fabric according to claim 53, in which the polymeric matrix comprises polyvinyl chloride or other non-flammable plastisol.

56. A fabric as claimed in any one of Claims 49 to 55 in which the ink comprises an ink as claimed in any one of Claims 1 to 17, 22 to 24, 39 or 46 to 48.